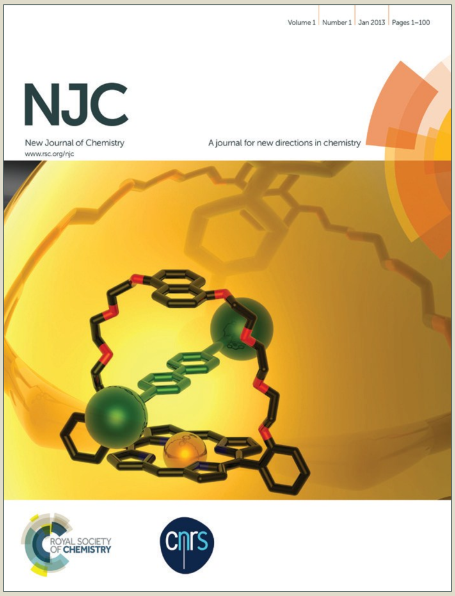
NJC

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: F. Panahi, N. Zarnaghash and A. Khalafi-Nezhad, *New J. Chem.*, 2015, DOI: 10.1039/C5NJ02409A.



View Article Online
DOI: 10.1039/C5NJ02409A

Journal Name

ARTICLE

Phosphanamine-functionalized magnetic nanoparticles (PAFMNP): an efficient magnetic recyclable ligand in Pd-catalyzed Heck reaction of chloroarenes

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Farhad Panahi,*[a] Narges Zarnaghash[a] and Ali Khalafi-Nezhad,*[a]

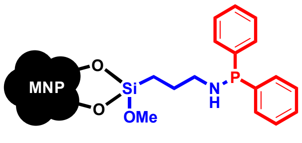
A phosphanamine-functionalized trimethoxysilyl compound (DPPPA) was synthesized and reacted with magnetic nanoparticles in order to synthesis a novel magnetic reusable phosphanamines ligand (PAFMNP) for application in transition metal-catalyzed coupling reactions. The Pd complex of PAFMNP (Pd-PAFMNP) was found to be an efficient heterogeneous catalyst in the Heck reaction of aryl chlorides. Only, 1.0 mol% of catalyst is needed to accomplish the Heck reaction of aryl chlorides. The catalyst was reusable at least for 5 times without significant decreasing in its catalytic activities.

Introduction

A remarkable development has recently been illustrated to improve highly reactive palladium catalysts for the Heck reactions of aryl chlorides.[1] The poor activity of aryl chlorides in coupling processes is due to their inherent unwillingness to oxidatively add to Pd(0) complexes. This limitation can be resolved using an active palladium catalyst system.[2] Nevertheless, there are few reactive catalyst systems which can perform the Heck reaction of aryl chlorides under relatively mild conditions.[1,3] A brief survey in the literature show that, most of the introduced active Pd catalyst systems are homogeneous with the assist of phosphorous or NHC ligands.[1,3,4]

Despite of the significant application of phosphorous ligands in transition-metal catalyzed organic reactions, they suffer from some disadvantages which limit their utilization. For example, most of the phosphorous ligands are easily oxidized by air (tendency in converting to phosphine oxides) and the reaction must be carried out under inert atmosphere, which strongly reduces the applicability of these ligands. High cost of producing, intrinsic toxicity, foul-smelling, difficulty of extraction and purification process and lack of recovery capability are other drawbacks of this valuable ligands.[5,6] The immobilization of phosphorus ligands on a solid support could help in solving some of the technical applications problems associated with them. Considering the aforementioned points there are numerous efforts on heterogenization of phosphorus ligands on different supports.[7]

One of the important classes of supports which used for synthesis of heterogeneous ligands and catalysts are magnetic nanoparticles (MNPs). This class of materials has considered as high surface area supports which are available, cheap, and stable for synthesis of heterogeneous catalyst systems.[8] Researches demonstrated that, by use of magnetic nanoparticles as support, reusability could be improved in comparison to other supports, because catalyst or ligand can be separated from the reaction mixture using an external magnetic field. The separation of catalyst using an external magnetic field not only improve the reusable capability of catalyst but it also make easy workup process.[9] Recently, our group reported on the development of magnetic reusable ligands and catalysts.[10] In continuation of our previous study we would like to introduce a magnetic recyclable phosphanamine ligand (PAFMNP) for application in transition metal catalyzed organic reactions (Figure 1). The applicability the PAFMNP ligand was evaluated in the heck reaction of chloroarenes.



PAFMNP

Figure 1. The chemical structure of phosphanamine-functionalized magnetic nanoparticles (PAFMNP)

The phosphanamines are now being widely used as ligands in the preparation of metallic complexes.[11] Phosphanamine are good candidates for application as efficient ligands in cross-coupling reaction. Since, the amino groups are strongly

---

[a] Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran
Emails: khalafi@chem.susc.ac.ir, panahi@shirazu.ac.ir
Fax: +98(713)2280926

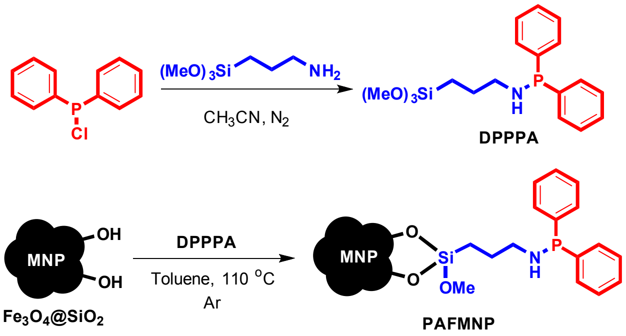
Electronic Supplementary Information (ESI) available: Experimental procedure and copy of ^{1}H NMR and ^{13}C NMR for all synthesized compounds. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C5NJ02409A

electron-donating making them stronger σ-donor ligands and so facilitating the easy oxidation of the transition metal. Also, the use of these electron-rich ligands accelerate the key oxidative addition step of the Pd-catalyzed coupling reactions.[12] It is well known that the P-N bond in phosphanamine is essentially a single bond, so the lone pairs on P are available for donor bonding towards metal atoms.[13]

Results and discussion

The synthetic route for the preparation of phosphanamines-functionalized magnetic nanoparticles (PAFMN) is shown in Scheme 1. One of the efficient methods for synthesis of phosphanamines is the aminolysis of halophosphanes which this approach was used in current study. [14] The reaction of chlorodiphenylphosphine ($ClPPh_2$) and 3-(trimethoxysilyl)propan-1-amine gave 1,1-diphenyl-*N*-(3-(trimethoxysilyl)propyl)phosphinamine (DPPPA). The synthesized DPPPA was characterized using ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, FT-IR and elemental analysis techniques and confirmed its successful synthesize (See supporting information). The DPPPA compound with a trimethoxysilyl group can easily and strongly connect to solid surface containing hydroxyl group toward synthesis of heterogeneous phosphanamine materials.



Scheme 1. Synthetic route toward synthesis of PAFMNP

In this study we decided to graft DPPPA to magnetic nanoparticles toward synthesis of a magnetic reusable phosphanamine ligand. Magnetic nanoparticles were prepared by co-deposition method using a procedure in the literature.[15] The synthesized magnetic nanoparticles (MNPs) were also coated by silica using a sol-gel process to obtain core-shell-MNPs ($Fe_3O_4@SiO_2$) which is containing larger hydroxyl groups in comparison with MNPs.[16] Treatment of DPPPA with $Fe_3O_4@SiO_2$, led to the formation of PAFMN ligand.

The prepared PAFMNP ligand was characterized using some different microscopic and spectroscopic techniques. A comparison between the FT-IR spectra of $Fe_3O_4@SiO_2$, DPPPA, and PAFMNP, reveals some absorption bands in the structure of PAFMN that confirm the supporting of DPPPA on MNPs (See supporting information). The transmission electron microscopy (TEM) images of the Pd-PAFMN catalyst show near to spherical nanoparticles with an average of 25 nm and good monodispersity (Fig. 2a, b & d). The scanning electron microscopy (SEM) image shows the morphology of PAFMNP ligand (Fig. 2c).

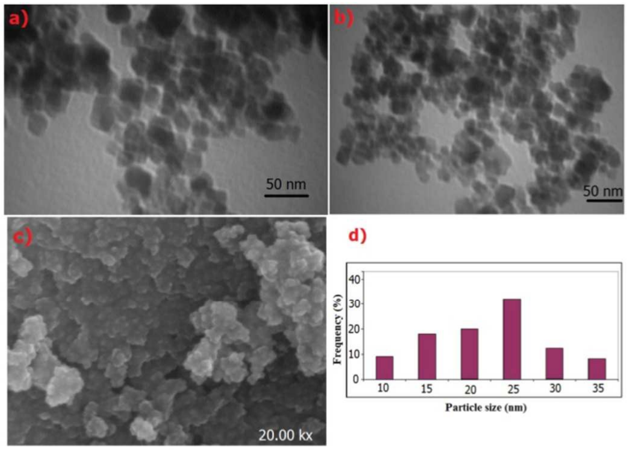


Figure 2. A TEM images of the PAFMNP ligand (a & b); A SEM image of PAFMNP ligand (c). A histogram representing the size distribution of PAFMNP nanoparticles (d)

In order to determine the amount of P atom on the surface of MNP, the PAFMNP ligand was analyzed by energy dispersive X-ray (EDX). The EDX spectra of the PAFMNP ligand (Fig. 3a) show the elements C, N, O, P, Si, and Fe. Based on the amount of 3.25% for P, it is possible to calculate the quantity of the grafted PPh_2 on the surface of magnetic nanoparticles which was equal to 1.05 mmol/g. Thermal gravimetric analysis (TGA) was applied to find the thermal stability and behavior of ligand.

The TGA analysis of the PAFMNP ligand (Fig. 3b) shows a ~4.4% weight loss until the temperature close to ~120 °C; this is due to the loss of absorbed water molecule. It also shows about 26.6 % weight loss at 180-310 °C, which is due to the decomposition of the grafted diphenylphosphine moiety. Moreover, the weight loss from 330-390 °C revealed the decomposition of the remained organic backbone.

The X-ray diffraction (XRD) pattern of PAFMN ligand is shown in Fig. 3c. The strongest peaks of the XRD pattern correspond to SiO_2 and other peaks are indexed as the (220), (311), (400), (422), (511) and (440) planes of the magnetic nanoparticles.[17]

The magnetic properties of the PAFMNP ligand were investigated at room temperature using a vibrating sample magnetometer (VSM). Based on the magnetization curve, the magnetization (Ms) is saturated up to 50 emu g^{-1} at an applied field of 8100 Oe (Fig. 3d). A comparison with the value of Ms (63.5) for pure Fe_3O_4 shows that PAFMNP particles are super paramagnetic.[18] The decrease of Ms value for PAFMNP can be attributed to the SiO_2 and organic layer in the structure of this material.

View Article Online
DOI: 10.1039/C5NJ02409A

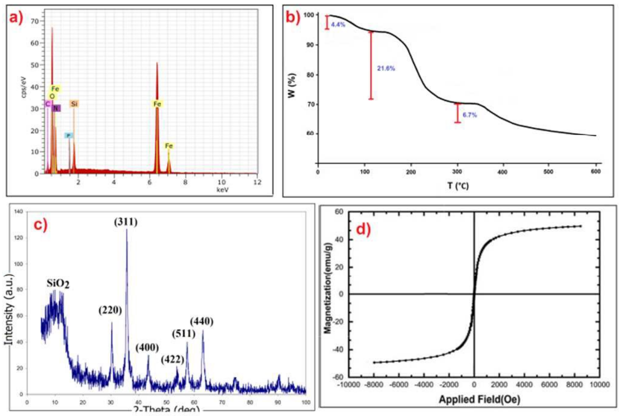
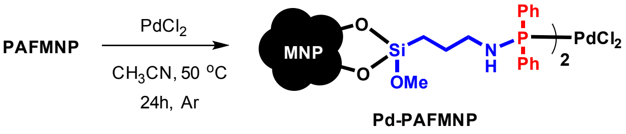


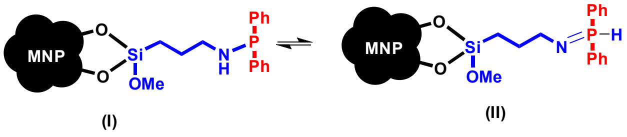
Figure 3. EDX (a), TGA (b), XRD (c) and VSM (d) of PAFMNP ligand

After characterization of PAFMNP ligand it was complexed with $PdCl_2$, resulted in the production of Pd-PAFMNP catalyst (Scheme 2).



Scheme 2. Synthesis of Pd-PAFMN catalyst

It should be mentioned that, phosphanamine (I) bearing protons at the nitrogen atom, may be involved in prototropic equilibrium with its phosphazene form (II) (Scheme 3).[19]



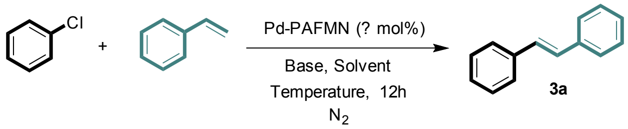
Scheme 3. The possible prototropic equilibrium between phosphanamine (I) and phosphazene (II) forms in PAFMNP ligand

The position of the equilibrium depends on the nature of the solvent and the substituents at the phosphorus and nitrogen atoms.[20] However, in complexation with metals such as Pd, phosphanamines coordinate *via* P atom (in phosphanamine form),[21] thus the proposed chemical structure for Pd-PAPMN catalyst showed in Scheme 2 is more possible.

The inductively coupled plasma (ICP) analysis shows that the amount of Pd in Pd-PAFMNP catalyst is 0.48 mmol/g. Thus, approximately, 2 groups of PPh_2 coordinated with each $PdCl_2$ (Scheme 2).

The first application of the Pd-PAFMNP was investigated in the Heck reaction of chloroarenes. The Pd-PAFMNP-catalyzed Heck reaction between chlorobenzene and styrene was selected as a model reaction to find optimum conditions by using change of solvent, base, temperature and catalyst loading (Table 1).

Table 1 Optimization of the Pd-PAFMN-catalyzed Heck Reaction between chlorobenzene and styrene [a]



Entry	Solvent	Base	Catalyst (mol%)	T/°C	Yield (%)[b]
1	DMF	K_2CO_3	1.5	120	91
2	NMP	K_2CO_3	1.5	120	86
3	DMSO	K_2CO_3	1.5	120	79
4	Toluene	K_3PO_4	1.5	110	78
5	Xylene	K_3PO_4	1.5	110	80
6	DMF	K_3PO_4	1.5	120	88
7	DMF	DBU	1.5	120	75
8	DMF	DABCO	1.5	120	77
9	DMF	Cs_2CO_3	1.5	120	90
10	DMF	K_2CO_3	1.2	120	91
11	DMF	K_2CO_3	1.0	120	90
12	DMF	K_2CO_3	0.8	120	83
13	DMF	K_2CO_3	1.0	120	91[c]
14	DMF	K_2CO_3	1.0	130	92
15	DMF	K_2CO_3	1.0	120	85[d]
16	DMF	K_2CO_3	1.0	120	89[e]
17	DMF	K_2CO_3	1.0	120	91[f]
18	DMF	K_2CO_3	1.0	120	92[g]

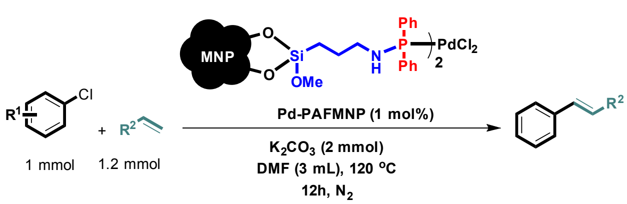
[a] Amount of materials in all reactions: chlorobenzene (1 mmol), styrene (1.2 mmol), base (2 mmol), solvent (3 mL), and under N_2 gas. [b] Yield of isolated **3a**. [c] Reaction time was 24h. [d] $Pd(OAc)_2/PPh_3$ was used as catalyst. [e] $Pd(PPh_3)_4$ was used as catalyst. [f] $PdCl_2(dppe)$ was used as catalyst. [g] $PdCl_2(dppf)$ was used as catalyst.

By selection of DMF as solvent, K_2CO_3 as base and in the presence of 1.5 mol% of Pd-PAFMNP catalyst about 91% of product **3a** was observed (Table 1, entry 1). Different solvents such as NMP, DMSO, toluene and xylene were also checked and no superiority was observed (Table 1, entries 2-5). Thus DMF was selected as solvent for this reaction. Then the type of base was changed and it was observed that K_2CO_3 is the best tested base for Heck reaction of aryl chlorides in the presence of Pd-PAFMNP catalyst (Table 1, entries 6-9). Next the catalyst loading was also optimized and 1 mol% of catalyst was recognized as optimum (Table 1, entries 10-12). By increasing the reaction time to 24h and temperature to 130 °C no improvement in reaction yield was observed (Table 1, entries 13 & 14). The efficiency of our catalyst system was compared with some of the commercially available Pd-catalytic system for Heck reaction of chloroarens (Table 1, entries 15-18). By use of $Pd(OAc)_2/PPh_3$ catalyst system only 85% of product was obtained. The $Pd(PPh_3)_4$ catalyst was checked and 89% of

View Article Online
DOI: 10.1039/C5NJ02409A

product was isolated from the reaction mixture. It should be mentioned that the efficiency of $PdCl_2$/dppe and $PdCl_2$/dppf catalyst system was not higher than the Pd-PAFMNP catalyst system. Thus, the Pd-PAFMNP catalyst is superior to some of the commercially available catalyst systems in term of reaction yield and conditions.

As optimum condition, the reaction was carried out in DMF solvent, using K_2CO_3 as base, at 120 °C (Scheme 4).



Scheme 4. The prototropic equilibrium between phosphanamine and phosphazene forms

Next, we examined the generality of the application of Pd-PAFMNP catalyst in the Heck reaction of aryl chlorides using other substrates (Figure 4).

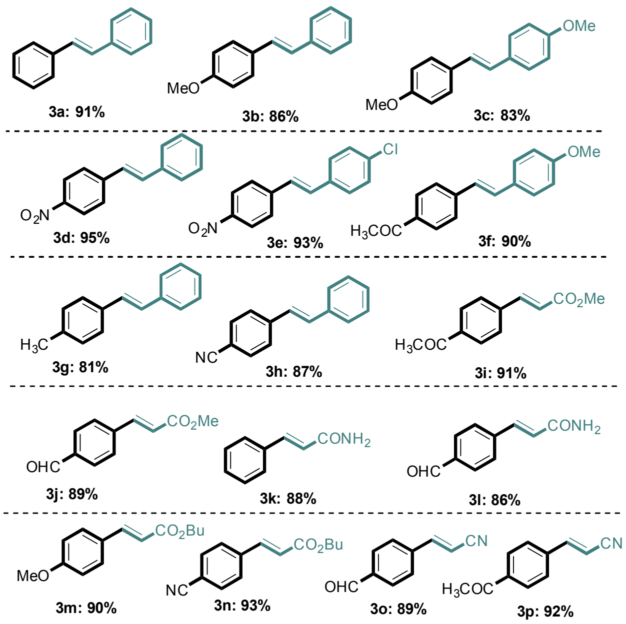
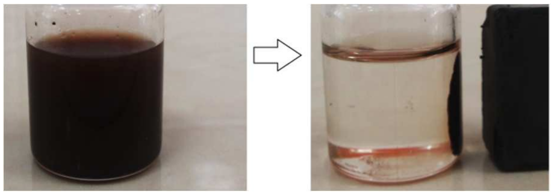


Figure 4. Heck reaction products synthesized by Pd-PAFMNP catalyst. Reaction conditions: chloroarene (1.0 mmol), alkene (1.2 mmol), K_2CO_3 (2.0 mmol), Pd-PAFMNP (1 mol%), DMF (3.0 mL), 120 °C and under N_2. Yields are isolated product.

According to the Fig. 4, all of the used aryl chlorides were readily coupled with styrenes in good to excellent yields. For example, with 4-chloroanisole and 4-chloronitrobenzene, up to 83% of products were obtained. 4-Chloroacetophenone, 4-chlorotoluene and 4-chlorobenzonitrile were also successfully applied and compounds **3f-h** were obtained in 81-91% yields. Thus, styrenes were efficiently undergone in the reaction with aryl chlorides under optimized conditions to give the corresponding stilbene products in good to excellent yields. Using methyl acrylate, Heck reaction of 4-chloroacetophenone and 4-chlorobenzaldehyde resulted in the production of **3i** (91%) and **3j** (89%), respectively. Interestingly, the presence of an amide group was well tolerated, as demonstrated with the synthesis of compounds **3k** and **3l** using acrylamide. To show the generality of this methodology further, butyl acrylate and acrylonitrile were used and compounds **3m-p** were obtained in excellent yield. It should be mentioned that, the *E* isomer of coupling products were observed.

The possibility of recycling of the catalyst was examined using the reaction of chlorobenzene and styrene under optimized reaction conditions. When the reaction was complete, the catalyst was separated using an external magnet, and the recycled catalyst was saved for the next run. The recycled catalyst could be reused more than five times without significant decreasing in its catalytic activity (Table 2).

Table 2 Reusability of the Pd-PAFMNP catalyst in the Heck reaction[a]



Entry	Yield of Product (%)[b]	Recovery of catalyst (%)
1	91	99
2	89	98
3	88	97
4	87	96
5	85	95

[a] Reaction conditions: chlorobenzene (1.0 mmol), styrene (1.2 mmol), K_2CO_3 (2.0 mmol), DMF (3.0 mL), 120 °C and under N_2.

To confirm this point, the catalyst activity of Pd-PAFMNP did not change remarkably during the reaction process; we checked the Pd content of the catalyst using ICP after 5 times of reusability and the results have shown that only 0.5% of Pd was lost.

The hot filtration test was also accomplished to clarify that leaching of Pd species from the catalyst and result of ICP analysis show that a negligible amount of Pd (less than 0.1% of Pd) was removed, demonstrating that catalyst act heterogeneous in practice. Also, the Heck reaction in DMF solvent after removing of catalyst failed to product, representing lack of Pd leaching and stability of catalyst system under this conditions.

Conclusions

In conclusion, we have developed an efficient method for the synthesis of a new magnetic reusable phosphorous ligand. The magnetic reusable phosphanamine ligand was synthesized using a simple procedure and cheap and available starting

View Article Online
DOI: 10.1039/C5NJ02409A

materials. We also report the preparation and utilization of a new and high performance magnetic nanoparticles supported Pd catalyst system for application in Heck reaction of chloroarenes as unactive substrates in this protocol. The magnetic nature of palladium complex of phosphanamine-functionalized magnetic nanoparticles facilitates its separation from the reaction mixture. Simple strategy of construction, high reactivity and easy workup process are other advantages of this catalyst system. Also, this ligand provides great promise toward further useful applications in other metal-catalyzed transformations in the future.

Experimental section

General. Chemicals were purchased from Merck and Aldrich Chemical Companies. For recorded ^{1}H-NMR and ^{13}C-NMR spectra we used Brucker (250 MHz) Advance DRX in pure deuterated DMSO-d_6 and $CDCl_3$ solvents with tetramethylsilane (TMS) as internal standards. The ^{31}P NMR spectrum of DPPPA was recorded on a Bruker Advance DPX 400 MHz spectrometer. FT-IR spectroscopy (Shimadzu FT-IR 8300 spectrophotometer), was employed for characterization of the compounds and catalyst. The transmission electron microscopy (TEM) was obtained using TEM apparatus (CM-10-philips, 100 kV) for characterization of the ligand. The scanning electron micrograph (SEM) for the PAMNP ligand was obtained by SEM instrumentation (SEM, XL-30 FEG SEM, Philips, at 20 kV). The thermogravimetry analysis (TGA) of the samples was analyzed using a lab-made TGA instrument. The X-ray diffraction (XRD, D8, Advance, Bruker, axs) was employed for characterization of the catalyst. ICP analysis was determined using an inductively coupled plasma (ICP) analyzer (Varian, Vista-Pro). Melting points were determined in open capillary tubes in a Barnstead Electrothermal 9100 BZ circulating oil melting point apparatus. The reaction monitoring was accomplished by TLC on silica gel PolyGram SILG/UV254 plates. Column chromatography was carried out on columns of silica gel 60 (70–230 mesh).

Synthesis of DPPPA, PFMNP ligand and of Pd-PFMNP catalyst

Synthesis of DPPPA. To a solution of chlorodiphenylphosphane (10 mmol) in CH_3CN (50 mL) were added 3-(trimethoxysilyl)propan-1-amine (10 mmol) and triethylamine (20 mmol). The solution was stirred at 80 °C for 12h under nitrogen atmosphere. The CH_3CN solvent was removed under vacuum and the crude solid was purified by column chromatography on silica gel using ethylacetate/*n*-hexane (1:3) as eluent to give a yellow viscous product. Yield: 2.5 g (70 %). IR (KBr): ν = 2399.3, 1905.5, 1833.0, 1712.7, 1666.4, 1589.2, 1434.9, 1265.2, 1183.1, 918.1, 825.5 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): 0.42 (brs, 2H), 1.47 (brs, 2H), 2.51 (brs, 2H), 3.16 (s, 9H), 7.03-7.54 (m, 10H), 8.10 (brs, 1H). ^{13}C-NMR (250 MHz, $CDCl_3$): 14.1, 22.7, 51.8, 52.6, 128.2, 128.4, 128.9, 129.0, 130.7, 130.8, 131.2, 131.3, 131.7, 132.3, 132.7, 133.7, 141.2. ^{31}P-NMR (162 MHz, $CDCl_3$): 21.68, 31.72. Anal. calcd for $C_{18}H_{26}NO_3PSi$ (363.47): C, 59.48; H, 7.21; N, 3.85. Found: C, 59.21; H, 7.09; N, 3.69.

Synthesis of magnetic nanoparticles (Fe_3O_4).[15] Magnetic nanoparticles were prepared via co-precipitation of Fe(III) and Fe(II) ions in the presence of sodium hydroxide. In a canonical flask, a mixture of $FeCl_2.2H_2O$ (16 mmol, 2.6 g) and $FeCl_3.6H_2O$ (30 mmol, 8.1 g) was dissolved in 100 mL of deionized water. Then, the pH of this solution was increased to 11 by adding a 3M solution of NaOH as drop wise (in a period of 5 min) at 40 °C. Subsequently, the temperature of mixture was enhanced to 80 °C and the solution was stirred for 20 min in this temperature. The magnetic nanoparticles as a dark solid were isolated from the solution by magnetic separation and washed with deionized water until pH 7 reached.

Synthesis of core-shell magnetic nanoparticles ($Fe_3O_4@SiO_2$).[16] $Fe_3O_4@SiO_2$ nanoparticles were prepared based on the literature with some modification: to a mixture of 250 mL of cyclohexane, 50 mL of 1-hexanol, 80 mL of triton X-100, and 25 mL of water, 2g of Fe_3O_4 was added. Then the mixture was stirred by mechanical stirrer under N_2 gas for 30 min. 20 mL of tetraethyl orthosilicate (TEOS) was added to the mixture next and then the solution was stirred for 12h at 28 °C. After the specified time, 18 mL of ammonia was added and the solution was stirred continuously for another 12h. The precipitation was washed with ethanol (3 x 10) and collected by external magnetic field. The desired product was dried under vacuum overnight.

Synthesis of PAFMNP ligand. PAFMNP was prepared according to the previous reported procedure in the literature. 0.5 g of $Fe_3O_4@SiO_2$ was suspended in a mixture of 100 mL dry toluene including (0.22 g, 0.6 mmol) of DPPPA. The mixture was refluxed under Ar atmosphere at 110 °C for 24 h. The PAFMNP was obtained as a dark solid using an external magnet after washing with ethanol and dried under vacuum for 12 h at 50 °C.

Synthesis of Pd-PFMNP catalyst. To a mixture of PAFMNP (2.5 g) in dry CH_3CN (30 mL), palladium chloride (237mg, 1.35 mmol) was added and stirred for 24 h at 50 °C under Ar gas. Then, the mixture was filtered and washed with dichloromethane (3 x 10 mL) and diethyl ether (2 x 10). After drying in a vacuum oven at 50 °C for overnight the Pd-PAFMN catalyst was obtained as a dark solid.

General procedure for Heck reaction in the presence of PFMNP catalyst. In a typical experiment, to a mixture of aryl chloride (1 mmol), acrylate/styrene (1.2 mmol), and K_2CO_3 (2 mmol) in 3 mL DMF, Pd-PAFMNP catalyst (0.02 g, 1 mol%) was added and heated in an oil bath at 120 °C under N_2 gas. The reaction was followed by TLC. After completion of the reaction, the mixture was cooled down to room temperature and the catalyst was separated from the reaction mixture using an external magnetic field and washed with diethyl ether (2 x 10 mL) followed by deionized and oxygen-free water (2 x 10 mL). The reused catalyst was dried for the next run. The organic phase after separation of catalyst was evaporated to obtain crude product. For further purification column chromatography was used.

View Article Online
DOI: 10.1039/C5NJ02409A

Acknowledgements

Financial support from the research councils of Shiraz University is gratefully acknowledged.

Notes and references

1 Please see some of the reactive Pd catalyst systems in the Heck reaction of aryl chlorides: (a) A. Ehrentraut, A. Zapf and M. Beller, *Synlett* 2000, 1589; (b) N. J. Whitcombe, K. K. Hii, S. E. Gibson, *Tetrahedron*, 2001, **57**, 7449; (c) A. F. Littke and G. C. Fu, *J. Am. Chem. Soc.*, 2001, **123**, 6989; (d) A. Schnyder, T. Aemmer, A. F. Indolese, U. Pittelkow and M. Studer, *Adv. Synth. Catal.* 2002, **344**, 495; (e) W. Kleist, S. S. Pröckl, K. Köhler, *Catal. Lett.* 2008, **125**, 197; (f) V. Calo, A. Nacci, A. Monopoli and P. Cotugno, *Angew. Chem. Int. Ed.* 2009, **48**, 6101; (g) C. Diebold, S. Schweizer, J. –M. Becht and C. L. Drian, *Org. Biomol. Chem.*, 2010, **8**, 4834; (h) H.-J. Xu, Y.-Q. Zhao and X.-F. Zhou, *J. Org. Chem.* 2011, **76**, 8036; (i) H.J. Xu, Y.Q. Zhao and X.F. Zhou, *J. Org. Chem.* 2011, **76**, 8036; (j) A. Ataei, S. Nadri, E. Rafiee, S. Jamali, M. Joshaghani, *J. Molecul. Catal. A.: Chem.* 2013, **366**, 30;

2 (a) V. V. Grushin and H. Alper. Activation of Otherwise Unreactive C-Cl Bonds. In: Murai S, editor. Activation of Unreactive Bonds and Organic Synthesis. Springer-Verlag; Berlin: 1999. pp. 193–226; (b) Y. -R. Luo. Handbook of Bond Dissociation Energies in Organic Compounds. CRC Press; New York: 2003; (c) Z.-J. Shi, Z.-X. Wang and W.-J. Guo, Homogeneous Catalysis for Unreactive Bond Activation. Chapter 1: Catalysis in C–Cl activation, 2014; (d) A. F. Littke and G. C. Fu, *Angew. Chem. Int. Ed. Engl.* 2002, **41**, 4176.

3 Please see the following examples: (a) C. Amatore, A. Jutand, *Acc. Chem. Res.* 2000, **33**, 314; (b) K. Selvakumar, A. Zapf and M. Beller, *Org. Lett.*, 2002, **4**, 3031; (c) S. S. Pröckl, W. Kleist, K. Köhler, *Tetrahedron*, 2005, **61**, 9855; (d) R. Srivastava, N. Venkatathri, D. Srinivas, P. Ratnasamy, *Tetrahedron Lett.* 2003, **44**, 3649; (e) D.-H. Lee, A. Taher, S. Hossain, and M.-J. Jin, *Org. Lett.* 2011, **13**, 5540

4 (a) S. S. Pröckl, W. Kleist, M. A. Gruber, K. Köhler, *Angew. Chem. Int. Ed.* 2004, **43**, 1881; (b) S. Demir, I. Özdemir, B. Çetinkaya, *Appl. Organomet. Chem.* 2006, **20**, 254; (c) J. Ruan, J. A. Iggo, N. G. Berry and J. Xiao, *J. Am. Chem. Soc.* 2010, **132**, 16689

5 W. A. Herrmann, *Angew. Chem. Int. Ed.* 2002, **41**, 1290.

6 (a) W. Tang, X. Zhang, *Chem. Rev.* 2003, **103**, 3029; (b) M. Doux, N. Mézailles, M. Melaimi, L. Ricard, P.L. Floch, *Chem. Commun.* 2002, 1566.

7 (a) X. Zhang, P. Li, Y. Ji, L. Zhang, L. Wang, *Synthesis* 2011, 2975; (b) M. Chen, F. Zhang and H.-X. Li, *Curr. Org. Chem.* 2013, **17**, 1051; (c) T. Iwai, T. Harada, K. Hara and M. Sawamura, *Angew. Chem., Int. Ed.* 2013, **52**, 12322; (d) A. F. Cardozo, E. Manoury, C. Julcour, J.-F. Blanco, H. Delmas, F. Gayet and R. Poli, *Dalton Trans.* 2013, **42**, 9148; (e) T. Shiomi, T. Nakahodo and H. Fujihara, *Chem. Lett.* 2012, **41**, 1700; (f) B. Ma, Z. Ding, J. Liu, Y. He and Q.-H. Fan, *Chem. –Asian J.* 2013, **8**, 1101; (g) T. Iwai, R. Tanaka, T. Harada and M. Sawamura, *Chem. Eur. J.* 2014, **20**, 1054; (h) T. Iwai, R. Murakami, T. Harada, S. Kawamorita and M. Sawamura, *Adv. Synth. Catal.* 2014, **356**, 1563; (i) S. Han, Y. Feng, F. Zhang, C. Yang, Z. Yao, W. Zhao, F. Qiu, L. Yang, Y. Yao, X. Zhuang and X. Feng, *Adv. Func. Matt.* 2015, **38**, 99.

8 (a) V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, and J. –M. Basset, *Chem. Rev.* 2011, **111**, 3036; (b) B. Karimi, F. Mansouri and H.M. Mirzaei, *ChemCatChem*, 2015, **7**, 1736.

9 (a) R. Mrówczyński, A. Nan and J. Liebscher, *RSC Adv.* 2014, **4**, 5927; M. B. Gawande, P. S. Branco and R. S. Varma, *Chem. Soc. Rev.* 2013, **42**, 3371.

10 (a) A. Khalafi-Nezhad, F. Panahi, *J. Organomet. Chem.* 2013, 741-742, 7; (b) A. Khalafi-Nezhad and F. Panahi *ACS Catal.* 2014, **4**, 1686; (c) A. Khalafi-Nezhad, M. Divar and F. Panahi, *RSC Adv.* 2015, **5**, 2223; (d) A. Khalafi-Nezhad, M. Nourisefat and F. Panahi, *RSC Adv.* 2014, 4, 22497; (e) A. Khalafi-Nezhad, M. Nourisefat and F. Panahi, *Org. Biomol. Chem.* 2015, **13**, 7772; (f) N. Zarnaghash, F. Panahi, A. Khalafi-Nezhad, *J. Iran Chem. Soc.* 2015, DOI: 10.1007/s13738-015-0682-0.

11 M. Alajarín, C. López-Leonardo, P. Llamas-Lorente, *Top Curr. Chem.* 2005, **250**, 77.

12 N, Miyaura, A. Suzuki, *Chem. Rev.* 1995, **95**, 2457.

13 (a) A.A. Korkin, E.N. Tsvetkov, Bull Soc. Chim. Fr. 1988, 2, 335; (b) D. Müller, L. Guénée, and A. Alexakis, *Eur. J. Org. Chem.* 2013, 6335; (c) J.-B. Langlois and A. Alexakis, *Chem. Commun.* 2009, 3868.

14 (a) Z. Fei, R. Scopelliti, P.J. Dyson, *Dalton Trans.* 2003, 2772; (b) Q. Zhang, G. Hua, P. Bhattacharyya, A.M.Z. Slawin, J.D. Woollins, *Dalton Trans*, 2003, 3250

15 D. Yuan, Q. Zhang, J. Dou, *Catal. Commun.* 2010, **11**, 606.

16 Y. Kang, L. Zhou, X. Li, J. Yuan, *J. Mater. Chem.* 2011, **21**, 3704.

17 C. Wang, H. Daimon, S. Sun, *Nano Lett.* 2009, **9**, 1493.

18 S. A. Kulkarni, P. S. Sawadh and P. K. Palei, *J. Korean Chem. Soc.* 2014, **58**, 100.

19 P.V. Sudhakar, K. Lammertsma, *J. Am. Chem. Soc.* 1991, **113**, 1899.

20 Z. Fei, R. Scopelliti, P.J. Dyson, *Inorg. Chem.* 2003, **42**, 2125.

21 M. Raab, A. Sundermann, G. Schick, A. Loew, M. Nieger, W.W. Schoeller, E. Niecke, *Organometallics,* 2001, **20**, 1770.

View Article Online
DOI: 10.1039/C5NJ02409A

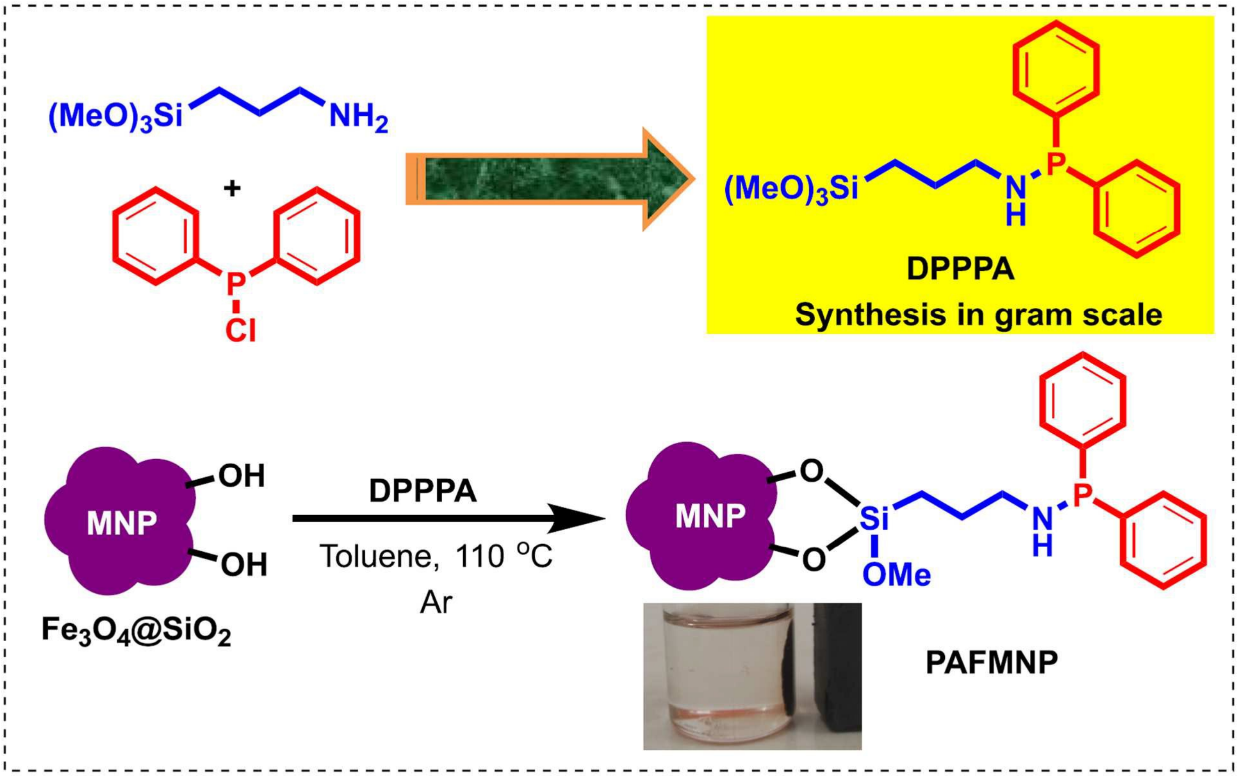
Phosphanamine-functionalized magnetic nanoparticles (PAFMNP): an efficient magnetic recyclable ligand in Pd-catalyzed Heck reaction of chloroarenes

Farhad Panahi,*[a] Narges Zarnaghasha and Ali Khalafi-Nezhad,*[a]

Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

Emails: khalafi@chem.susc.ac.ir, panahi@shirazu.ac.ir

Fax: +98(713)2280926



Reaction of MNPs with a phosphanamine-functionalized trimethoxysilyl compound resulted in the production of a novel and efficient magnetic reusable ligand for application in the Heck reaction of aryl chlorides.